# Exact asymptotics for non-radiative migration-accelerated energy transfer in one-dimensional systems.

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## Abstract

We study direct energy transfer by multipolar or exchange interactions between diffusive excited donor and diffusive unexcited acceptors. Extending over the case of long-range transfer of an excitation energy a non-perturbative approach by Bray and Blythe [Phys. Rev. Lett. **89**, 150601 (2002)], originally developed for contact diffusion-controlled reactions, we determine exactly long-time asymptotics of the donor decay function in one-dimensional systems.

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## I. INTRODUCTION

Long-range non-radiative transfer of an excitation energy from excited donor molecules to acceptors of the excitation energy is a dominant reaction mechanism in various chemical, physical and biological processes [1, 2, 3, 4, 5]. To name but a few, we mention fluorescence, luminescence or phosphorescence quenching, decay of trapped electrons in glassy media in presence of scavengers, or light harvesting by antennae chlorophyll-b molecules and donation of singlet energy to the chlorophyll-a reaction centers in photosynthetic organisms.

The idea of direct non-radiative transfer has been put forward in the pioneering works of Förster [6] and Dexter [7], who determined decay of an immobile excited donor due to dipole-dipole interactions with immobile, randomly placed acceptors in rigid three-dimensional solutions. Subsequent analysis (see Refs.[8] and references therein) extended the consideration of Förster and Dexter to arbitrary Euclidean dimensions $d$ and to general forms of donor-acceptor interactions, such as isotropic multipolar interactions, for which the rate $W(r)$ of energy transfer is given by

$$W(r) = \alpha_m \left(\frac{r_0}{r}\right)^n , \tag{1}$$

or interactions mediated by exchange, for which one has

$$W(r) = \alpha_e \exp\left(-\gamma r\right), \tag{2}$$

where $r$ is the distance separating a given donor-acceptor pair, the constants $n$, $r_0$ and $\gamma$ determine the interaction type and range (e.g., $n = 6$ for dipolar, $n = 10$ for quadrupolar interactions).

Note that an exponential form in Eq.(2) emerges, as well, in another important area - outer sphere electron transfer reactions. Kinetics of such electron tunneling processes taking place in liquids or glassy media have been also widely studied giving rise to a very beneficial crossfertilization of ideas and approaches.

For the transfer rates in Eqs.(1) and (2), it was found [8] that the probability $P(t)$ that the donor is still in excited state up to time $t$ obeys, at sufficiently long times,

$$P(t) \sim \exp\left[-V_d \Gamma(1 - d/n) n_A r_0^d \left(\alpha_m t\right)^{d/n}\right] \tag{3}$$

for multipolar and

$$P(t) \sim \exp\left[-V_d \gamma^{-d} n_A \ln^d\left(\alpha_e t\right)\right] \tag{4}$$

for exchange-mediated transfer, respectively. In Eqs.(3) and (4), $n_A$ denotes mean density of acceptor molecules, $V_d = \pi^{d/2}/\Gamma(1 + d/2)$ and $\Gamma(x)$ is a Gamma-function. The decay forms in

Eqs.(3) and (4) have been also generalized for certain types of restricted geometries - fractals [9], porous [4, 9, 10, 11] and various microheterogeneous [12] media as well as polymer solutions [13, 14].

However, in many situations the donors and acceptors are not immobile. In liquids, both donor and acceptor molecules perform diffusive motion. In solids, excitations become delocalized because of incoherent hopping between donor sites, which ultimately results in a diffusive transport, although the decay kinetics may be still different from that predicted for conventional diffusive motion - there always exists a finite probability that an excitation remains on an intitially excited donor [15, 16].

It was recognized [17] that random migration of donor and acceptor molecules leads to a much more efficient deactivation than the direct transfer between the immobile species; in three-dimensions, in particular, one finds that $P(t)$ obeys [17]

$$P(t) \sim \exp\left[-4\pi \left(D_A + D_D\right) R_{\text{eff}} n_A t\right], \tag{5}$$

where $D_D$ and $D_A$ are donor and acceptor diffusion coefficients and $R_{\text{eff}}$ is the effective reaction radius.

Note that the result in Eq.(5) has been first obtained for $W(\rho)$ in Eq.(1) with $n = 6$ and $D_A = 0$ in Ref.[18], which analyzed the relaxation of the nuclear magnetization in the presence of paramagnetic impurities. Recently, the result in Eq.(5) has been generalized to 3D systems with donors and acceptors performing anomalous, "fractional" diffusion [19].

To the best of our knowledge, there do not exist analogous results for low-dimensional, (i.e. 1D and 2D) systems, although the extension of the approach of Refs.[17] for 1D and 2D situations seems to be straightforward. In doing so, one will find

$$P(t) \sim \exp\left[-n_A \phi(t)\right], \tag{6}$$

where $\phi(t) \sim ((D_A + D_D)t)^{1/2}$ in 1D and $\phi(t) \sim (D_A + D_D)t/\ln((D_A + D_D)t)$ in 2D.

On the other hand, it is clear that neither Eq.(5) nor Eq.(6) is an exact solution for the long-range energy transfer problem involving diffusive donor and acceptor molecules, but a result of a certain assumption. While particles' diffusion coefficients will indeed appear only in the form of a sum $D_A + D_D$ in the solution of a problem with a single donor and a single acceptor, it is not the case in the general situation with a concentration of acceptor molecules. In particular, setting $D_A = 0$, one should obtain a crossover to a singular behavior characterized by a stretched-exponential time dependence $\ln P(t) \sim -t^{d/(d+2)}$ [20], whereas Eq.(5) does not show any singularity in the limit $D_A \to 0$.

Apart of this, it was recently discovered [21] that, remarkably, for diffusion-controlled contact $C + B \to B$ reactions taking place in low dimensional systems (or, generally, in dimension $d \leq d_f$, where $d_f$ is fractal dimension of particles' trajectories in case of subdiffusive motion [23]), the long-time asymptotical form of $P(t)$ is *independent* of the $C$ particle diffusion coefficient.

In this paper we extend the non-perturbative approach of Bray and Blythe [21] developed originally for contact diffusion-controlled reactions to systems with diffusive donor and acceptors interacting via distance-dependent isotropic multipolar or exchange transfer rates in Eqs.(1) and (2). We define, in form of convergent in the limit $t \to \infty$ upper and lower bounds, the exact form of the excitation survival probability $P(t)$ in one-dimensional systems. More specifically, we show that in 1D systems, both for multipolar and exchange-mediated transfer $P(t)$ obeys

$$1 + O\left(\frac{1}{t^{1/2}}\right) \leq \frac{\ln P(t)}{-4n_A\sqrt{D_A t/\pi}} \leq 1 + O\left(\frac{1}{t^{1/6}}\right). \tag{7}$$

This exact result proves that, in contrast to predictions based on standard considerations, Eqs.(6), the donor decay function in 1D is independent of donor's diffusion coefficient in the asymptotic regime. Remarkably, the decay forms appear to be *exactly* the same as for *contact* diffusion-controlled trapping reactions, (such that reaction takes place upon encounters between particles), [21] despite the fact that in our case reaction proceeds via *long-range* transfer rates in Eqs.(1) and (2) and encounters between particles do not lead to any particular reaction event.

In a separate publication [24], we proceed to show that this is also true for two-dimensional systems, while in 3D one may obtain a fluctuation-induced lower bound on the decay function which, in some range of parameters, is better (higher) than predictions based on standard Smoluchowski approach, Eq.(5).

This paper is outlined as follows. In Section II we define the model and introduce basic notations for the general $d$-dimensional case. In Section III we derive a general upper bound on the global decay function, while section IV presents the derivation of the lower bound. Next, in Sections V and VI, focusing on a 1D case, we evaluate the bounds on the global decay functions eplicitly for exchange-mediated and multipolar transfer, respectively, and demonstrate that they coincide in the asymptotic limit $t \to \infty$ defining in such a way an asymptotically exact result. Finally, in Section VII we conclude with a brief recapitulation of our results and an outlook for future work.

## II. MODEL AND BASIC EQUATIONS

Consider a $d$-dimensional spherical volume $V$ containing a single excited donor molecule, which is initially located at the origin, and $K$ acceptor molecules, placed at random positions. Suppose that both donor and acceptors perform conventional diffusive motion with diffusion coefficients $D_D$ and $D_A$, respectively. Let the instantaneous positions of the donor and of the acceptors be denoted by the ($d$-dimensional) vectors $\mathbf{r}(t)$ and $\mathbf{R}_k(t)$, $k = 1, 2, \ldots, K$.

We will neglect here the backtransfer to the donor. This neglect is well justified if the donor-acceptor energy difference is much larger than $k_BT$, $T$ being temperature and $k_B$ the Boltzmann constant. We also disregard here donor-specific radiative and radiationless processes. These decay channels are independent of the direct energy transfer and thus the overall donor decay function factorizes into the product of the donor-specific decay law, $\exp(-t/\tau_R)$, where $\tau_R$ is the rate of the donor-specific decay, times the acceptor determined decay function. Thus we focus here only on the non-radiative donor-acceptor transfer.

One assumes the acceptors to act independently, which means that they contribute multiplicatively to the decay. This assumption is well fulfilled when the density of acceptors is low. Under such an assumption, the probability that the donor is still in excited state at time $t$, for a given realization of its trajectory $\mathbf{r}(t)$ and given realizations of acceptors' trajectories $\{\mathbf{R}_k(t)\}$, is given by

$$P(\mathbf{r}(t), \{\mathbf{R}_k(t)\}) = \prod_{k=1}^{K} \exp\left[-\int_0^t W(\rho_k(t'))dt'\right], \tag{8}$$

where $\rho_k$ denotes the separation distance between the donor and $k$-th acceptor.

Experimentally measured property is the global decay function averaged over all possible donor and acceptor trajectories

$$P(t) = E_0^D\left\{\left\langle \prod_{k=1}^{K} E^A_{\mathbf{R}_k(0)}\left\{\exp\left[-\int_0^t W(\rho_k(t'))dt'\right]\right\}\right\rangle_{\mathbf{R}_k(0)}\right\}, \tag{9}$$

where the symbol $E_0^D\{...\}$ denotes averaging with respect to all possible donor's trajectories $\mathbf{r}(t)$; symbols $E^A_{\mathbf{R}_k(0)}\{...\}$ denote averaging with respect to the trajectories of the k-th acceptor, commencing its motion at position $\mathbf{R}_k(0)$, and finally, the angle brackets stand for the averaging with respect to the distribution of the starting positions. Note that presenting $P(t)$ in the form as in Eq.(9), we have already implicitly assumed that all acceptors move independently of each other, which is again well-justified for sufficiently low acceptor concentrations.

After some straightforward calculations, we arrive at the following thermodynamic-limit expression:

$$P(t) = E_0^D \left\{ \exp \Big[ - n_A Q(\mathbf{r}(t); t) \Big] \right\} \tag{10}$$

where $n_A$ is the mean concentration of acceptor molecules, ($n_A = K/V$ when both $K, V \to \infty$), while $Q(\mathbf{r}(t); t)$ is the following functional of a given donor trajectory $\mathbf{r}(t)$:

$$Q(\mathbf{r}(t); t) = \int d\mathbf{R}(0) E^A_{\mathbf{R}(0)} \left\{ 1 - \exp \left[ - \int_0^t dt' W(|\mathbf{r}(t') - \mathbf{R}(t')|) \right] \right\} \tag{11}$$

In the latter equation, $\mathbf{R}(t)$ denotes a given trajectory of a single acceptor molecule and $E^A_{\mathbf{R}(0)} \{...\}$ denotes averaging over all possible trajectories $\mathbf{R}(t)$. Note that straightforward averaging in Eqs.(10) and (11) is a non-tractable mathematical problem since averaging over acceptor trajectories in Eq.(11) has to be taken first for a *given* realization of donor's trajectory and only after doing it, one may perform averaging of the exponential in Eq.(10). Consequently, a recourse has to be made to approximations.

## III. UPPER BOUND ON THE GLOBAL DECAY FUNCTION: PASCAL PRINCIPLE

A convenient for our purposes upper bound on the global decay function stems from the so-called Pascal principle, which in our terms can be formulated as follows: an excitation on an immobile donor molecule survives longer than on a randomly moving one. In other words, $P(t)$ in Eq.(10) is bounded by

$$P(t) \leq P_u(t), \tag{12}$$

where $P_u(t)$ describes the decay of an immobile donor, fixed at the origin, due to a concentration $n_A$ of *diffusive* acceptor molecules,

$$P_u(t) = \exp \left[ -n_A \int d\mathbf{R}(0) E^A_{\mathbf{R}(0)} \left\{ 1 - \exp \left[ - \int_0^t dt' W(|\mathbf{R}(t')|) \right] \right\} \right] \tag{13}$$

The inequality in Eq.(12) has been first conjectured in Ref.[21] for contact trapping reactions and proven in Ref.[22] for one-dimensional systems. In Ref.[25], Eq.(12) has been proven for a rather general class of random walks on $d$-dimensional lattices. We also remark that a similar statement has been proven earlier in Ref.[15] for the process of an excitation energy migration via distance-dependent transfer rates on a disordered array of immobile donor molecules and quenched by randomly placed immobile acceptors. It was shown that the survival probability of an excitation

can be only decreased because of random motion not correlated with acceptors' spatial distribution. However, no rigorous proof of such a statement exists at present for diffusion-controlled long-range reactions although it is intuitively clear that the inequality in Eq.(12) should hold in this case too. We thus assume, without proof, that the inequality in Eq.(12) is also valid for the model under study.

Next, applying Feynmann-Kac theorem [27, 28] one may show that

$$E^A_{\mathbf{R}(0)}\left\{\exp\left[-\int_0^t dt' W(|\mathbf{R}(t')|)\right]\right\} = \int d\mathbf{R} G_t(\mathbf{R}|\mathbf{R}(0)), \tag{14}$$

$G_t(\mathbf{R}|\mathbf{R}(0))$ being the Green's function solution of the following Schrödinger equation:

$$\begin{aligned} \frac{\partial}{\partial t} G_t(\mathbf{R}|\mathbf{R}(0)) &= D_A \triangle_{\mathbf{R}} G_t(\mathbf{R}|\mathbf{R}(0)) - W(|\mathbf{R}|) G_t(\mathbf{R}|\mathbf{R}(0)), \\ G_{t=0}(\mathbf{R}|\mathbf{R}(0)) &= \delta(\mathbf{R} - \mathbf{R}(0)), \end{aligned} \tag{15}$$

where $\triangle_{\mathbf{R}}$ is a $d$-dimensional Laplace operator.

Note that Eqs.(15) presumes that donor and acceptors are point-like, non-interacting particles. In reality, they possess hard-cores and can not approach each other at distance less than $a$, equal to the sum of donor and acceptor radii. This means that Eqs.(15) are to be complemented by a reflective boundary condition at $|\mathbf{R}| = a$ [2].

Taking advantage of Eqs.(14) and (15), we can formally rewrite Eq.(13) as

$$P_u(t) = \exp\left[n_A \int_0^t dt' \int d\mathbf{R}\, \frac{\partial G_{t'}(\mathbf{R})}{\partial t'}\right],\ G_t(\mathbf{R}) = \int d\mathbf{R}(0) G_t(\mathbf{R}|\mathbf{R}(0)). \tag{16}$$

Assuming next that $G_t(\mathbf{R})$ is independent of angular variables such that $G_t(\mathbf{R}) = G_t(r)$, where $r = |\mathbf{R}|$, we get the following compact expression:

$$P_u(t) = \exp\left[-n_A \int_0^t dt' k_u(t')\right], \tag{17}$$

in which equation $k_u(t)$ is determined by

$$k_u(t) = d\, V_d \int_a^\infty r^{d-1} W(r) G_t(r), \tag{18}$$

and $G_t(r)$ obeys

$$\begin{aligned} \frac{\partial G_t(r)}{\partial t} &= D_A \left(\frac{\partial^2 G_t(r)}{\partial r^2} + \frac{d-1}{r}\frac{\partial G_t(r)}{\partial r}\right) - W(r) G_t(r), \\ G_{t=0} &= 1; \quad G_t(r \to \infty) = 1, \quad \left.\frac{\partial G_t(r)}{\partial r}\right|_{r=a} = 0. \end{aligned} \tag{19}$$

Equations (17), (18) and (19) thus define the upper bound on the global decay function $P(t)$ in systems with diffusive donor and acceptors.

## IV. LOWER BOUND ON THE GLOBAL DECAY FUNCTION.

We turn now to the derivation of a lower bound on $P(t)$ in Eq.(10). Following Ref.[21] (see also Ref.[26]), we make the following steps:

(i) suppose that for a given initial placement of acceptors, a closest to the origin acceptor appears at distance $l$. Thus, a notional spherical volume $V_l$ of radius $l$, centered at the origin, is initially completely devoid of acceptors.

(ii) performing averaging over donor's trajectories $\{\mathbf{r}(t)\}$, we consider only such trajectories which never leave $V_l$ up to time moment $t$. Since $Q(\mathbf{r}(t);t)$ in Eq.(11) is always positive definite for any particular realization $\mathbf{r}(t)$, such a constraint naturally leads to a lower bound on $P(t)$, i.e.

$$E_0^D\left\{\exp\Big[-n_A Q(\mathbf{r}(t);t)\Big]\right\} \geq E^D_{0,\mathbf{r}(t)\in V_l}\left\{\exp\Big[-n_A Q(\mathbf{r}(t);t)\Big]\right\}, \tag{20}$$

where $E^D_{0,\mathbf{r}(t)\in V_l}\{...\}$ denotes averaging over a subset of all possible donor's trajectories such that they do not leave $V_l$ during time $t$.

(iii) considering the term responsible for long-range transfer, $Q(\mathbf{r}(t);t)$, we suppose that the donor is always located on the surface of $V_l$ at position *closest* to the instantaneous position of the acceptor. Since $W(\rho)$ is a strictly decreasing function of $\rho$, for any $r(t)\in V_l$, one has $W(|\mathbf{R}(t)|-l)\geq W(|\mathbf{r}(t)-\mathbf{R}(t)|)$ and hence, $Q(\mathbf{r}(t);t)$ can be majorized by

$$Q(\mathbf{r}(t);t)\leq Q(l;t)=\int d\mathbf{R}(0)E^A_{\mathbf{R}(0)}\left\{1-\exp\left[-\int_0^t dt' W(|\mathbf{R}(t')|-l)\right]\right\} \tag{21}$$

Note now that the right-hand-side of the inequality in Eq.(21) is *independent* of the donor's trajectories.

Consequently, collecting (i) to (iii), we arrive at the following *lower* bound on the global decay function

$$P(t)\geq P_{\rm void}(l)\ \times E^D_{0,\mathbf{r}(t)\in V_l}\{1\}\ \times\exp\left[-n_A R(l;t)\right]. \tag{22}$$

In this equation $P_{void}(l)$ is the probability of having an acceptor-free spherical void of radius $l$. For random intial placement of acceptors, one has

$$P_{\rm void}(l)\sim\exp\Big[-n_A V_d\, l^d\Big]. \tag{23}$$

Further on, in Eq.(22) the symbol $E^D_{0,\mathbf{r}(t)\in V_l}\{1\}$ denotes the measure of such donor's trajectories, which commence at the origin and never leave $V_l$ during time $t$; at sufficiently large times, $E^D_{0,\mathbf{r}(t)\in V_l}\{1\}$ is given by

$$E^D_{0,\mathbf{r}(t)\in V_l}\{1\}\sim\exp\left[-z_d^2\frac{D_D t}{l^2}\right], \tag{24}$$

$z_d$ being the first zero of the Bessel function $J_{(d-2)/2}(x)$.

Combining the expressions in Eqs.(23) and (24), and assuming spherical symmetry, we finally obtain

$$P(t) \geq P_l(t) = \exp\left[-n_A V_d l^d - z_d^2 \frac{D_D t}{l^2} - n_A \int_0^t dt' k_l(t')\right]. \tag{25}$$

In the latter equation,

$$k_l(t) = d\, V_d \int_{l+a}^{\infty} r^{d-1} W(r-l) \tilde{G}_t(r) dr, \tag{26}$$

while $\tilde{G}_t(r)$ is the solution of

$$\begin{aligned} \frac{\partial \tilde{G}_t(r)}{\partial t} &= D_A \left( \frac{\partial^2 \tilde{G}_t(r)}{\partial r^2} + \frac{d-1}{r} \frac{\partial \tilde{G}_t(r)}{\partial r} \right) - W(r-l)\tilde{G}_t(r), \\ \tilde{G}_{t=0}(r) &= 1; \quad \tilde{G}_t(r \to \infty) = 1, \end{aligned} \tag{27}$$

subject, in virtue of condition (iii), to a reflection boundary condition imposed at $r = l + a$:

$$\left. \frac{\partial \tilde{G}_t(r)}{\partial r} \right|_{r=l+a} = 0. \tag{28}$$

Equations (25),(26),(27) and (28) define a family of lower bounds on the global decay function in systems with diffusive donor and acceptors, dependent on the radius $l$ of the notional volume $V_l$ encircling the donor and devoid of acceptors.

To get the optimal lower bound, we will have, in the usual fashion, to maximize the result with respect to $l$. Below we consider lower and upper bounds on the global decay function in one-dimensional systems with long-range transfer (Eqs.(1) and (2)) between diffusive donor and diffusive acceptors. Corresponding results for two- and three-dimensional systems will be presented elsewhere [24].

## V. ONE-DIMENSIONAL SYSTEMS: EXCHANGE-MEDIATED TRANSFER.

### A. Upper bound.

Consider first the derivation of *an upper bound* in one-dimensional systems with a transfer mediated by exchange. Here, Laplace-transformed with respect to time variable $t$, solution of Eqs.(27) and (28) reads:

$$\begin{aligned} G_\lambda(r) &= \int_0^\infty dt \exp[-\lambda t] G_t(r) = C_1 I_\chi(x) + C_2 K_\chi(x) + \\ &+ \frac{\chi \Gamma(1-\frac{\chi}{2})}{\lambda} \left(\frac{x}{2}\right)^{\frac{\chi}{2}} \int_0^1 I_{-\frac{\chi}{2}}(x\xi)\, \xi^{1+\frac{\chi}{2}} \left(1-\xi^2\right)^{\frac{\chi}{2}-1} d\xi, \end{aligned} \tag{29}$$

where $K_\chi(x)$ and $I_\chi(x)$ are modified Bessel functions, the integral term in the second-line is a particular solution (Lommel function) and

$$x = \omega \exp[-\gamma \frac{r}{2}], \quad x_0 = \omega \exp[-\gamma \frac{a}{2}], \quad \omega = \frac{2}{\gamma}\sqrt{\frac{\alpha_e}{D_A}}, \quad \text{and} \quad \chi = \frac{2}{\gamma}\sqrt{\frac{\lambda}{D_A}}. \tag{30}$$

Now, note that as $r \to \infty$, $x \to 0$, $I_\chi(x) \to 0$, the last term on the rhs of Eq.(29) tends to $1/\lambda$, while $K_\chi(x)$ diverges. Hence, we set $C_2 = 0$. Further, we get that the reflective boundary condition at the closest approach distance is fulfilled when

$$C_1 = -\frac{2\chi\Gamma(1-\frac{\chi}{2})}{\lambda\left(I_{\chi-1}(x_0)+I_{\chi+1}(x_0)\right)}\left(\frac{x_0}{2}\right)^{\frac{\chi}{2}}\int_0^1 I_{1-\frac{\chi}{2}}\left(x_0\xi\right)\xi^{2+\frac{\chi}{2}}\left(1-\xi^2\right)^{\frac{\chi}{2}-1}d\xi \tag{31}$$

Plugging Eqs.(29) and (31) into Eq.(18) and performing intergation, we find that the Laplace-transformed reaction constant $k_u(\lambda)$ is given by

$$\begin{aligned} k_u(\lambda) \;=\; & \frac{D_A\gamma x_0^2}{\lambda}\Big[\,{}_2F_3\left(1,1;2,1-\frac{\chi}{2},1+\frac{\chi}{2},\frac{x_0^2}{4}\right) - \frac{2}{(1+\frac{\chi}{2})(1-\frac{\chi^2}{4})\Gamma(1+\chi)}\times \\ & \times\;\left(\frac{x_0}{2}\right)^{1+\chi}\frac{{}_1F_2\left(2;2-\frac{\chi}{2},2+\frac{\chi}{2};\frac{x_0^2}{4}\right)\;{}_1F_2\left(1+\frac{\chi}{2};2+\frac{\chi}{2},1+\chi;\frac{x_0^2}{4}\right)}{I_{\chi-1}\left(x_0\right)+I_{\chi+1}\left(x_0\right)}\Big], \end{aligned} \tag{32}$$

where ${}_pF_q$ denote generalized hypergeometric functions.

Leading small-$\lambda$ (large-$t$) asymptotic behavior of $k_u(\lambda)$ in Eq.(32) follows

$$k_u(\lambda) \sim 2\sqrt{\frac{D_A}{\lambda}}\frac{1}{1+\sqrt{T_e\lambda}}, \tag{33}$$

where

$$T_e = \left(\frac{K_1\left(x_0\right)+\left(1/2-C+\ln\left(2/x_0\right)\right)I_1\left(x_0\right)}{I_1\left(x_0\right)}\right)^2\frac{4}{\gamma^2 D_A}, \tag{34}$$

$C \approx 0.577$ being the Euler constant.

This yields, in $t$-domain, the following asymptotical behavior

$$\int_0^t dt' k_u(t') = 4\sqrt{\frac{D_A t}{\pi}}\left(1-\sqrt{\frac{\pi T_e}{4t}}+O\left(\frac{1}{t}\right)\right) \tag{35}$$

Consequently, in 1d systems with transfer mediated by exchange we have the following upper bound on the global decay function:

$$P(t) \le \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}}+2n_A\sqrt{D_A T_e}+O\left(\frac{1}{t^{1/2}}\right)\right] \tag{36}$$

Before we proceed to the derivation of the lower bound, a few comments are in order:

(a) first of all, we notice that the right-hand-side of Eq.(36) coincides with the solution of the

so-called target problem - probability that an immobile target survives, in one dimension, up to time $t$ in presence of diffusive scavengers which may "destroy" the target upon the first encounter with it [29]. Therefore, in one dimension, at sufficiently long times the kinetic behavior of long-range transfer proceeds exactly in the same way as for contact diffusion-limited target annihilation reaction, despite the fact that here the boundary condition imposed on the donor's surface is reflective and the deactivation of the donor happens, at rate $\alpha_e \exp(-\gamma r)$, at any donor-acceptor distance $r$.

(b) parameter $T_e$ in Eq.(34) is the crossover time to the asymptotic stage $\ln P_u(t) \sim -t^{1/2}$ for exchange-mediated transfer in one-dimensional systems with immobile donor and mobile acceptors. Note that $\gamma^2 D_A T_e$ is a non-monotonic function of $x_0$. It is large $\sim 1/x_0^4$ when $x_0 \ll 1$ (i.e., when $D_A$ is large), such that $T_e \sim \gamma^2 D_A/\alpha_e^2$. In this case, one would first observe, for $0 < t < T_e$, an intermediate asymptotical behavior $\ln P(t) \sim -\gamma\alpha t$, which will then cross to the asymptotical behavior in Eq.(36). Next, note that $\gamma^2 D_A T_e$ is also large when $x_0 \gg 1$, which happens when $D_A$ is small. Here, $T_e \approx \ln^2(x_0/2)/\gamma^2 D_A$, i.e. $T_e$ is proportional to the first inverse power of $D_A$ (with logarithmic corrections). In this case, the asymptotic decay in Eq.(36) succeeds the static quenching decay in Eq.(4), which is valid in progressively larger time domain the closer $D_A$ is to zero.

(c) finally, we remark that despite the fact that the result in Eq.(35) is independent of both $\alpha_e$ and $\gamma$, which are the only parameters characterizing the transfer rate and thus "represent" reaction, it does not mean that it can be simply obtained by expanding $G(r) = \sum_{n=0}^{\infty} \alpha_e^n G_n(r)$ and considering the zeroth term only. In general, Eq.(35) is essentially a non-perturbative result and can not be obtained using a perturbative expansion of $G_t(r)$ in powers of $\alpha_e$, unless, of course, one manages to sum the whole series. On the other hand, Eq.(35) can be straightforwardly derived approximating the transfer rate by a step-function ("square well" approximation).

Indeed, suppose that $\gamma a < 1$ and consider separately solution of Eqs.(27) and (28) for $a \leq r \leq 1/\gamma$ and $r \geq 1/\gamma$. In the first interval we approximate $\exp[-\gamma r]$ by $\exp[-\gamma a]$, and find that the Laplace-transformed solution of the Schrödinger equation which obeys the reflecting boundary condition reads

$$G_\lambda^{(1)} = \frac{1}{\lambda + \alpha_e \exp[-\gamma a]} + C_1 \cosh\left[\sqrt{\frac{\lambda + \alpha_e \exp[-\gamma a]}{D_A}}(r-a)\right] \tag{37}$$

On the other hand, in the domain $r \geq 1/\gamma$, the transfer term can be neglected, and we have

$$G_\lambda^{(2)}(r) = \frac{1}{\lambda} + C_2 \exp\left[-\sqrt{\frac{\lambda}{D_A}}\left(r - \frac{1}{\gamma}\right)\right] \tag{38}$$

Since $G_\lambda(r)$ and its first derivative have to be continuous functions at $r = 1/\gamma$, we have two complementary equations which define the coefficients $C_1$ and $C_2$. Determining these coefficients, we find that the leading small-$\lambda$ behavior of $k_u(\lambda)$ follows

$$k_u(\lambda) \;=\; 2\alpha_e \exp\left[-\gamma a\right] \int_a^{1/\gamma} G_\lambda^{(1)}(r) dr = 2\sqrt{\frac{D_A}{\lambda}} \frac{1}{1+\sqrt{T_e'\lambda}}, \tag{39}$$

where

$$T_e' = \frac{\exp[a\gamma]}{\alpha_e} \coth^2\left(\frac{x_0}{2}\right). \tag{40}$$

Note that $k_u(\lambda)$ in Eq.(39) has exactly the same form as $k_u(\lambda)$ in Eq.(33), which means that the "square well" approximation captures well the leading behavior of the effective reaction rate. The crossover time $T_e'$ has a different form compared to the exact one, Eq.(34); it exhibits, however, quite a "correct" behavior in the case $x_0 \ll 1$ (fast diffusion) when $T_e' \sim \gamma^2 D_A/\alpha_e^2$.

### B. Lower bound.

Consider now a lower bound on $P(t)$ for one-dimensional systems with transfer mediated by exchange interactions. Laplace-transformed solution of Eqs.(27) and (28) reads

$$\tilde{G}_\lambda(r) = C_1 I_\chi(xe^{\frac{\gamma l}{2}}) + \frac{\chi\Gamma(1-\chi/2)}{\lambda}\left(\frac{xe^{\frac{\gamma l}{2}}}{2}\right)^{\frac{\chi}{2}} \int_0^1 I_{-\frac{\chi}{2}}\left(x\xi e^{\frac{\gamma l}{2}}\right) \xi^{1+\frac{\chi}{2}} \left(1-\xi^2\right)^{\frac{\chi}{2}-1} d\xi, \tag{41}$$

where $C_1$ is given by Eq.(31). Plugging the expression in Eq.(41) into Eq.(26) and performing integration, we find that $k_l(\lambda)$ obeys

$$k_l(\lambda) \equiv k_u(\lambda), \tag{42}$$

where $k_u(\lambda)$ is determined by Eq.(32). Consequently, the lower bound on $P(t)$, Eq.(25), at sufficiently long times attains the following form:

$$P_l(t) \sim \exp\left[-2n_A l - \pi^2 \frac{D_D t}{l^2} - 4n_A\sqrt{\frac{D_A t}{\pi}}\right] \tag{43}$$

As we have already mentioned, the result in Eq.(43) represent rather a family of lower bounds dependent on parameter $l$ - radius of a notional volume initially devoid of acceptors. The "best" lower bound thus would be the highest one. Optimizing Eq.(43) with respect to $l$, we find that the highest lower bound is achieved when $l = (\pi^2 D_D t/n_A)^{1/3}$, and is given by

$$P_{l,max}(t) \sim \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}} - 3n_A^{2/3}\left(\pi^2 D_D t\right)^{1/3}\right] \tag{44}$$

On comparing the asymptotic behavior predicted by the maximal lower bound in Eq.(44) against the upper bound in Eq.(36) we notice that both bounds converge asymptotically to give an exact result in Eq.(7).

## VI. ONE-DIMENSIONAL SYSTEMS: MULTIPOLAR TRANSFER.

### A. Upper bound.

Consider now, within the "square well" approximation, an upper bound in case of multipolar transfer in Eq.(1). Approximating the actual transfer rate $W(r)$ in Eq.(1) by a step-function

$$W(r) = \begin{cases} \alpha_m (r_0/a)^n, a \le r \le r_0, \\ 0, \quad r \ge r_0 \end{cases}$$

we find that in the interval $a \le r \le r_0$ Laplace-transformed solution of Eq.(19) obeys

$$G_\lambda^{(1)} = \frac{1}{\lambda + \alpha_m (r_0/a)^n} + C_1 \cosh\left[\sqrt{\frac{\lambda + \alpha_m (r_0/a)^n}{D_A}}(r-a)\right], \tag{45}$$

while in the domain $r \ge r_0$ it follows

$$G_\lambda^{(2)}(r) = \frac{1}{\lambda} + C_2 \exp\left[-\sqrt{\frac{\lambda}{D_A}}\,(r-r_0)\right]. \tag{46}$$

Constants $C_1$ and $C_2$ are to be chosen in such a way that both $G_\lambda(r)$ and its first derivative are continuous functions at $r = r_0$.

Determining these constants, plugging Eq.(45) into Eq.(18) and performing integration, we find that the Laplace-transformed $k_u(t)$ is given by

$$k_u(\lambda) = 2\sqrt{\frac{D_A}{\lambda}}\left(1 + \sqrt{\frac{\lambda a^n}{\alpha_m r_0^n}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0 - a)\right)\right)^{-1} + \frac{2\alpha_m (r_0/a)^n (r_0 - a)}{\lambda + \alpha_m (r_0/a)^n} \tag{47}$$

This yields, in $t$-domain,

$$\int_0^t k_u(t')dt' = 4\sqrt{\frac{D_A t}{\pi}}\left(1 - \sqrt{\frac{\pi a^n}{4\alpha_m r_0^n\, t}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0 - a)\right) + O\left(\frac{1}{t}\right)\right). \tag{48}$$

Consequently, the global decay function $P(t)$ in one-dimensional systems with diffusive donor and acceptors interacting via multipolar transfer rate in Eq.(1) is bounded from above by

$$P(t) \le \exp\left[-4n_A\sqrt{\frac{D_A t}{\pi}} + 2n_A\sqrt{\frac{D_A a^n}{\alpha_m r_0^n}}\coth\left(\sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}}(r_0 - a)\right)\right]. \tag{49}$$

### B. Lower bound.

Turning next to evaluation of the lower bound on $P(t)$ we introduce parameter $\delta > a$, and approximate the actual transfer rate by a step-function of the form

$$W(r) = \begin{cases} \alpha_m (r_0/a)^n, l + a \le r \le l + \delta, \\ 0, \quad r \ge \delta \end{cases}$$

Approximate solution of Eqs.(27) in the interval $l + a \le r \le l + \delta$ has the form

$$\tilde{G}_\lambda^{(1)} = \frac{1}{\lambda + \alpha_m (r_0/a)^n} + C_1 \cosh \left[ \sqrt{\frac{\lambda + \alpha_m (r_0/a)^n}{D_A}} (r - l - a) \right], \tag{50}$$

while in the domain $r \ge l + \delta$ it is given by

$$\tilde{G}_\lambda^{(2)}(r) = \frac{1}{\lambda} + C_2 \exp \left[ -\sqrt{\frac{\lambda}{D_A}} \, (r - l - \delta) \right]. \tag{51}$$

Again, requiring continuity of $\tilde{G}_\lambda(r)$ and of its first derivative at $r = l + \delta$, we determine $C_1$ and $C_2$, which yields, after straightforward calculations, the following expression

$$k_l(\lambda) = 2\sqrt{\frac{D_A}{\lambda}} \left( 1 + \sqrt{\frac{\lambda a^n}{\alpha_m r_0^n}} \coth \left( \sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}} (\delta - a) \right) \right)^{-1} + \frac{2\alpha_m (r_0/a)^n (\delta - a)}{\lambda + \alpha_m (r_0/a)^n}, \tag{52}$$

We find then that in the $t$-domain, the leading behavior of $\int_0^t k_l(t')dt'$ is given by

$$\int_0^t k_l(t')dt' = 4\sqrt{\frac{D_A t}{\pi}} - 2\sqrt{\frac{D_A a^n}{\alpha_m r_0^n}} \coth \left( \sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}} (\delta - a) \right) + O\left( \frac{1}{t^{1/2}} \right) \tag{53}$$

Consequently, an optimized lower bound on $P(t)$ reads

$$P(t) \ge \exp \left[ -4n_A \sqrt{\frac{D_A t}{\pi}} - 3n_A^{2/3} \left( \pi^2 D_D t \right)^{1/3} + 2n_A \sqrt{\frac{D_A a^n}{\alpha_m r_0^n}} \coth \left( \sqrt{\frac{\alpha_m (r_0/a)^n}{D_A}} (\delta - a) \right) \right] \tag{54}$$

On comparing the results in Eqs.(49) and (54), we notice that again both bounds converge as $t \to \infty$ determining exact asymptotic decay of the excited donor, Eq.(7).

## VII. CONCLUSIONS

To conclude, we have studied analytically direct energy transfer between diffusive excited donor and diffusive unexcited acceptors mediated by multipolar or exchange interactions. Extending a

non-perturbative approach by Bray and Blythe [21] (originally developed for contact diffusion-controlled reactions) over the case of long-range transfer, we have determined exactly long-time asymptotics of the donor decay function in one-dimensional systems. We have shown that the leading long-time behavior is independent of the diffusion constant $D_D$ of the donor molecule, and has exactly the same form as that descibing contact process. This finding is in aparent contradiction with the results in Eqs.(5) and (6).

We proceed to show elsewhere [24] that also in two-dimensional systems the leading long-time behavior will be independent of $D_D$, while in 3D a similar approach will give rise to a fluctuation-induced lower bound on the decay function which, in some range of parameters, is better (higher) than predictions based on standard Smoluchowski approach.

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[1] S.A.Rice, *Diffusion-Limited Reactions*, in: C.H.Bamford, C.F.H.Tipper, R.G.Compton (Eds), Comprehensive Chemical Kinetics, Vol. **25** (elsevier, Amsterdam, 1985)

[2] A.I.Burshtein, Sov. Phys. Usp. **27**, 579 (1984)

[3] M.Graetzel, *Heterogeneous Photochemical Electron Transfer*, (CRC Press, Boca Raton, FL, 1989)

[4] J.Klafter and J.M.Drake (Eds.) *Molecular Dynamics in Restricted Geometries*, (Wiley, New York, 1989)

[5] A.V.Barzykin, P.A.Frantsuzov, K.Seki and M.Tachiya, Adv. Chem. Phys. **123**, 511 (2002)

[6] T.Förster, Z. Naturforsh. Teil A **4**, 321 (1949)

[7] D.L.Dexter, J. Chem. Phys. **21**, 836 (1953)

[8] see, e.g., M.Inokuti and F.Hirayama, J. Chem. Phys. **43**, 1978 (1965); M.Tachiya and A.Mozumder, Chem. Phys. Lett. **28**, 87 (1974); A.Blumen and R.Silbey, J. Chem. Phys. **70**, 3707 (1979)

[9] A.Blumen, J.Klafter and G.Zumofen, in *Optical Spectroscopy of Glasses*, Ed. I.Zschokke, (Reidel, Dordrecht, 1986), p.199

[10] P. Levitz and J. M. Drake, Phys. Rev. Lett. **58**, 686 (1987)

[11] J. M. Drake et al., Phys. Rev. Lett. **61**, 865 (1988)

[12] A.V.Barzykin, K.Seki and M.Tachiya, Adv. Colloid Interface Sci. **89**, 47 (2001).

[13] O. Pekcan, M.A.Winnik and M.D.Croucher, Phys. Rev. Lett. **61**, 641 (1988); A.Moeglich, K.Joder and T.Kiefhaber, PNAS **103**, 12394 (2006)

[14] A. K. Roy and A. Blumen, J. Chem. Phys. **91**, 4353 (1989); S.F.Burlatsky, G.S.Oshanin, and A.V.Mogutov, Phys. Rev. Lett. **65**, 3205 (1990); G. Oshanin, A. Blumen, M. Moreau, and S. F. Burlatsky, J. Chem. Phys. **103**, 9864 (1995); J.H.Kim and S.Lee, J. Chem. Phys.**119**, 11957 (2003); R.Reigada and I.M.Sokolov, Macromolecules **38**, 3504 (2005)

[15] S.F.Burlatsky, G.Oshanin and A.A.Ovchinnikov, Phys. Lett. A **139**, 241 (1989)

[16] S.G.Fedorenko, A.I.Burshtein and A.A.Kipriyanov, Phys. Rev. B **48**, 7020 (1993)

[17] see, e.g., M.Yokota and O.Tanimoto, J. Phys. Soc. Jpn **22**, 779 (1967); I.Z.Steinberg and E.Katchalski, J. Chem. Phys. **48**, 404 (1968); M.J.Pilling and S.A.Rice, J. Chem. Soc. Faraday Trans. **72**, 792 (1976); U.Gösele, M.Hauser, U.K.A.Klein and R.Frey, Chem. Phys. Lett. **34**, 519 (1975); K.Allinger and A.Blumen, J. Chem. Phys. **72**, 4608 (1980); B.Sipp and R.Voltz, J. Chem. Phys. **79**, 434 (1983)

[18] P.-G.de Gennes, J. Phys. Chem. Solids **7**, 345 (1958)

[19] K.Seki, A.I.Shushin, M.Wojcik and M.Tachiya, J. Phys. Cond. Mat. **19**, 065117 (2007)

[20] L.A.Pastur, Theor. Math. Phys. **32**, 88 (1977)

[21] A.J.Bray and R.A.Blythe, Phys. Rev. Lett. **89**, 150601 (2002); Phys. Rev. E **67** 041101 (2003)

[22] A.J.Bray, S.N.Majumdar and R.A.Blythe, Phys. Rev. E **67**, 060102R (2003)

[23] G.Oshanin, O.Bénichou, M.Coppey, and M.Moreau, Phys. Rev. E **66**, 060101 (2002); S.B.Yuste and K.Lindenberg, Phys. Rev. E **72**, 061103 (2005); S.B.Yuste, J.J.Ruiz-Lorenzo, and K.Lindenberg, Phys. Rev. E **74**, 046119 (2006); S.B.Yuste, G.Oshanin, K.Lindenberg, O.Bénichou and J.Klafter, Survival probability of a particle in a sea of mobile traps: A tale of tails, arXiv:0805.2920, appearing in PRE

[24] G.Oshanin and M.Tachiya, in preparation

[25] M.Moreau, G.Oshanin, O.Bénichou and M.Coppey, Phys. Rev. E **67**, 045104R (2003); Phys. Rev. E **69**, 046101 (2004)

[26] S.Redner and K.Kang, J. Phys. A **17**, L451 (1984)

[27] R.P.Feynmann and A.Hibbs, *Quantum mechanics and path integrals*, (McGraw-Hill, New York, 1965)

[28] M.Kac, *Probability and related topics in physical sciences*, (Interscience, London, 1959)

[29] M.Tachiya, Radiat. Phys. Chem. **21**, 167 (1983); A.Blumen, G.Zumofen and J.Klafter, Phys. Rev. B **30**, 5379 (1984); A.Szabo, R.Zwanzig and N.Agmon, Phys. Rev. Lett. **61**, 2496 (1988); S.F.Burlatsky, M.Moreau, G.Oshanin and A.Blumen, Phys. Rev. Lett. **75**, 585 (1995); D.P.Bhatia, M.A.Prasad and D.Arora, **75**, 586 (1995); O.Bénichou, M.Moreau and G.Oshanin, Phys. Rev. E **61**, 3388 (2000).